Supplement of Atmos. Meas. Tech., 8, 2715–2736, 2015
http://www.atmos-meas-tech.net/8/2715/2015/
doi:10.5194/amt-8-2715-2015-supplement

Atmospheric Measurement Techniques
Open Access

Supplement of

ACTRIS non-methane hydrocarbon intercomparison experiment in Europe to support WMO GAW and EMEP observation networks

C. C. Hoerger et al.

Correspondence to: S. Reimann (stefan.reimann@empa.ch)

1. Methods

1.1 Expanded uncertainty determination of NMHC measurements

In order to have comparable uncertainty calculations for all measurements, all participants were asked to submit their results with expanded combined uncertainties (with coverage factor k=2), determined following the concept of the "Guide to the Expression of Uncertainty in Measurements" (JCGM, 2008).

The combined expanded uncertainty $\Delta\chi_{systematic}$ includes both the random errors described by the precision and the systematic errors $\Delta\chi_{systematic}$ of the measurement.

$$\Delta\chi^2_{unc} = \Delta\chi^2_{prec} + \Delta\chi^2_{systematic} \quad (1)$$

The precision for measured mole fractions is calculated as follows:

$$\Delta\chi_{prec} = \tfrac{1}{3} DL + \chi * \sigma^{rel}{}_{\chi_{sample}} \quad (2)$$

where DL = detection limit, χ = mole fraction of considered peak, and $\sigma^{rel}{}_{\chi_{sample}}$ = relative standard deviation of the sample.

Briefly, systematic errors comprise the error $\Delta\chi_{cal}$ due to uncertainty of the calibration standard's mole fractions, systematic integration errors (due to peak overlay or poor baseline separation) in $\Delta\chi_{\text{int}}$, systematic errors due to blank correction $\Delta\chi_{blank}$, and potential further instrumental problems $\Delta\chi_{instrument}$ (e.g. sampling line artefacts, possible non-linearity of the MS detector, changes of split flow rates).

Following Gaussian error propagation, the overall systematic error $\Delta\chi_{systematic}$ is then described as

$$\Delta\chi^2_{systematic} = \Delta\chi^2_{cal} + \Delta\chi^2_{\text{int}} + \Delta\chi^2_{blank} \left(+ \Delta\chi^2_{instrument}\right) \quad (3)$$

The systematic error $\Delta\chi_{cal}$ due to the calibration gas uncertainty is calculated as follows:

$$\Delta\chi_{cal} = \frac{A_{sample} * V_{cal}}{V_{sample} * A_{cal}} * \delta\chi_{cal} \quad (4)$$

where A_{sample} = peak area of sample measurement, A_{cal} = peak area of the calibration standard measurement, V_{sample} = sample volume of sample, V_{cal} = sample volume of calibration standard, and $\delta\chi_{cal}$ = certified standard uncertainty of calibration standard and potential drift of the calibration standard.

The systematic integration errors include

$$\Delta\chi^2_{\text{int}} = \left(\frac{f_{cal}}{V_{sample}} * \delta A_{sample}\right)^2 + \left(\frac{A_{sample} * V_{cal} * \chi_{cal}}{V_{sample} * A^2_{cal}} * \delta A_{cal}\right)^2 \text{ with } f_{cal,i} = \frac{V_{cal} * \chi_{cal}}{A_{cal}} \quad (5)$$

where χ_{cal} = mole fraction of calibration standard peak, δA_{cal} = integration error of calibration standard measurement, and δA_{sample} = integration error of the sample measurement.

For Equation 10 the sample mole fractions are calculated according to:

$$\chi = \frac{A_{sample} * V_{cal}}{V_{sample} * A_{cal}} * \chi_{cal} \quad (6)$$

The systematic integration error is determined by the partial derivatives $\frac{\partial \chi}{\partial A_{sample}}$ and $\frac{\partial \chi}{\partial A_{cal}}$ with

$$\frac{\partial \chi}{\partial A_{sample}} = \left(\frac{V_{cal} * \chi_{cal}}{V_{sample} * A_{cal}} \right) \text{ and } \frac{\partial \chi}{\partial A_{cal}} = \left(- \frac{A_{sample} * V_{cal} * \chi_{cal}}{V_{sample} * A_{cal}^2} \right) \quad (7)$$

Combining both errors by Gaussian error propagation yields

$$\Delta \chi_{\text{int}}^2 = \left(\frac{f_{cal}}{V_{sample}} * \delta A_{sample} \right)^2 + \left(\frac{A_{sample} * V_{cal} * \chi_{cal}}{V_{sample} * A_{cal}^2} * \delta A_{cal} \right)^2 \quad (8)$$

It should be pointed out that this error does not reflect random integration errors like small baseline differences but errors due to systematic structures in the baseline or peak-overlaps. In this case, systematic over- or underestimation of the peak area may occur. In the guideline provided for the participants, they were asked to assess reasonable systematic uncertainties based on reasonable assumptions about base line structure and peaks in the overlap area. If that was not possible they were asked to estimate the maximum systematic errors in a worse case assessment of such effects. We want to emphasize here that the repeatability of the peak area does not account for a systematic bias due to such problems. In fact, a "wrong" peak area might be determined with excellent repeatability. Thus, it is considered essential to introduce a systematic peak integration error.

If a blank correction has to be applied, the error of this correction is described as the deviation from the mean blank value:

$$\Delta \chi_{blank} = \sigma_{blank} * \frac{1}{\sqrt{n-1}} \quad (9)$$

where the standard deviation σ_{blank} is calculated from *n* zero-gas measurements. For more details and examples for the calculation of the different errors see ACTRIS VOCs measurement guidelines (http://www.actris.net/Portals/97/Publications/quality%20standards/WP4_D4.9_M42_30092014.pdf).

1.2 Determination of assigned values (error-weighted means) for NMHC mixtures

Based on the measurements of three reference laboratories (WCC-VOC, HPB and Empa), NMHC mole fractions for the NMHC mixtures were usually assigned as error-weighted means (Barlow, 1989;

Bronštejn, 2007), using the uncertainties u_i of the individual measurements as weight $w_i = 1/u_i^2$ and calculating the mean value X as follows:

$$X_{error-weighted} = \sum(w_i * x_i) / \sum(w_i) \quad (10)$$

where x_i = measured value and i = 1…n with n = number of measurements.

For the uncertainty of the error-weighted mean, an internal and external uncertainty needs to be distinguished. If values by similar GC instruments with similar systematic uncertainty are combined (e.g two measurements of the same instrument), the uncertainty of the error weighted mean corresponds to the internal uncertainty:

$$u_{internal} = 1/\sqrt{\sum(w_i)} \quad (11)$$

However, for different GC systems with different systematic uncertainties (here, the measurements of three different reference systems), the external uncertainty $u_{external}$ is used, which is calculated as weighted deviation from the weighted mean value

$$u_{external} = \sqrt{\left(\sum(w_i * (x_i - X)^2)/\left((n-1) * \sum(w_i)\right)\right)} \quad (12)$$

where n = number of measurements.

Since deviations from the mean may accidentally be very small, we estimate the uncertainty of the error-weighted mean to be the maximum of the respective internal and external uncertainty. To obtain the expanded uncertainty of the error-weighted mean, the uncertainty value was multiplied by two (coverage factor k=2, corresponding to 2 σ or roughly a 95% confidence interval).

For 1,3-butadiene and isoprene the mole fractions in NMHC_air declined from the start to the end of the intercomparison by on average 21% and 41%, respectively. Thus, for 1,3-butadiene and isoprene instead of the error-weighted mean, the arithmetic mean of the measurement was used:

$$X_{arithmetic} = (\sum(x_i))/n, \quad (13)$$

with a standard uncertainty of :

$$u_{arithmetic} = \sqrt{\frac{\sum(x_i - X)^2}{n-1}} \quad (14)$$

The measurements of the three laboratories agreed within 3% and 5% for NMHC_N_2 and NMHC_air, respectively. Exceptions to this were ethylbenzene (up to 8% in NMHC_N_2), *o*-xylene (up to 9% in NMHC_N_2 and 8% in NMHC_air), and 2,2-dimethylbutane (up to 15% in NMHC_air).

2. GC Results

In Tables S1-S2 information on the station and the instrument performing this intercomparison are summarized. Tables S3-S6 and Figures S1-S4 show the ACTRIS intercomparison results in different presentations and detail for those readers more interested in specific details. Table S7 lists the mean blank values reported by the participants.

Good chromatography with respect to peak shapes and resolution enables good results and vice versa. AUC and HAR have an identical instrument set-up but the chromatogram for the PLOT-column of AUC showed no baseline separation and many C_2-C_6-hydrocarbon-peaks tailed (Figure S5a). In contrast, HAR has a good chromatographic resolution of these compounds on the PLOT-column (Figure S5b). These substantial differences in the chromatography are due to column degradation in case of AUC. For NMHC in air, KOS_A achieved no baseline resolution for methane, ethane, and ethene which led to overestimated ethane mole fraction due to peak overlap (Figure S5c). This effect was not observed in the similar system of PAL (Figure S5d) due to a much longer initial hold time at 40°C of 15 min compared to only 5 min for KOS_A. Also, results by FZJ_B showed substantial deviations from the assigned values for the C_2-C_4 alkanes in both NMHC mixtures due to non-baseline separation (not shown here) which were related to aging effects of the column and solved by column replacement.

3. PTR-MS

3.1 Instrumentation

The proton transfer reaction mass spectrometer (PTR-MS, Ionicon Analytik GmbH, Austria) is described in detail by Lindinger et al. (1998), de Gouw et al. (2003), Warneke et al. (2003), de Gouw and Warneke (2007) and the used instrument calibration and data processing method by Taipale et al. (2008). In brief, the air samples are directly fed to the PTR-MS (Ionicon Analytik GmbH, Austria, Table S2a-b) without any drying or other pretreatments. The volatile organic compounds (VOCs) are ionized in a proton transfer reaction with hydronium ions (H_3O^+). The PTR-MS consists of three parts: a discharge ion source to produce the primary ions, a drift-tube reactor, and a quadrupole mass spectrometer for detecting primary and product ions. The H_3O^+ ions are produced in a hollow discharge cathode from pure water vapor and guided to the reaction chamber through a small orifice. The air sample is fed continuously through the drift tube, where the VOCs of the air sample collide with the H_3O^+ ions. If the proton affinity of the VOCs is higher than that one of water, the VOCs are ionized. The H_3O^+ ion performs a non-dissociative proton transfer to a majority of the VOCs. The mole fractions of a target compound were determined from the signal intensity at a specific mass to charge ratio (m/z). Fragmentation or charge transfer from O_2^+ ion was not taken into account. After the drift tube, the ions are guided to a quadrupole mass spectrometer for the selection and detection of the

ions. The instrument measures with one Thomson (Th) resolution, thus different compounds with same nominal m/z cannot be distinguished.

The instrument of SMR II was calibrated using a VOC calibration standard (Apel-Riemer Environment Inc., Table S2a-b) and VOC free air generated from ambient air with a catalytic converter. The calibration standard was diluted to a mole fraction of a few tens of nmol/mol. The instrumental background of the PTR-MS was determined by measuring VOC free air, and the background signals were subtracted from the measured signals. In the WCC-VOC the PTR-MS was calibrated using three dry gas standards in the low nmol/mol range (D64 1904: 28 hydrocarbon species with amount fractions of about 1 nmol/mol; D64 1977: 17 component monoterpene mixture with benzene, toluene and isoprene, amount fractions about 2 nmol/mol; D838784R: 29 NMHC mixture, amount fractions about 4 nmol/mol; balance gas: nitrogen; National Physical Laboratory (NPL), UK, Central Calibration Laboratory for Non-Methane Hydrocarbons of WMO-GAW).

3.2 Results and Discussion

SMEAR II (SMR II, Hyytiälä, Finland), and WCC-VOC (Garmisch-Partenkirchen, Germany) (Figure 1, main paper), reported mole fractions for m/z 69 (parent ion for isoprene), m/z 79 (parent ion for benzene), and m/z 93 (parent ion for toluene and p-cymene) (Figure S6). For the NMHC_N_2, m/z 69, WCC-VOC reported an amount fraction well within the ACTRIS data quality objective for isoprene (DQOs, Table 2, main paper), whereas for the NMHC_air a strong overestimation was observed. SMEAR II did not report isoprene. For m/z 93 and m/z 79 the results for both mixtures and for both stations were outside ACTRIS (5%-class) and former GAW DQOs (15%) for toluene and benzene, respectively.

The differences to the assigned values in two NMHC mixtures (NMHC_N_2 and NMHC_air) may be attributed to the lack of compound specificity of the PTR-MS analytical system (Blake et al., 2009). It is well known in mass spectroscopy that a detected m/z may be a result of different ions (parent ions, clusters, fragments). In the NMHC_N_2 sample m/z 69 seem to represent isoprene as assigned and measured values are very close as shown by WCC-VOC. In NMHC_air, however, m/z 69 is most likely a mixture of different ions.

An ion screening of the NMHC_air by PTR-MS analysis spanning a m/z range from 21 to 161 performed by WCC-VOC revealed a huge amount of oxygenated VOC present in the gas cylinder. Compared to back ground air, amount fraction m/z 59 (e.g. parent ion for acetone or propanal) was doubled, m/z 33 (parent ion for methanol) was higher by a factor of 4.5, m/z 45 (e.g. parent ion for acetaldehyde) was increased by a factor of about 10. Amount fractions of other oxygenated VOC with m/z 43 (e.g. parent ion for propanol) and m/z 61 (e.g. parent ion for acetic acid) were 60 times and 200 times higher, respectively, as in background air. It is very likely that also for m/z 69 other compounds (e.g. pentanal) as isoprene were co-detected and thus the reported value was the amount fraction of

alcohols or aldehydes rather than isoprene. In further GC-MS studies the exact composition of oxygenated VOC present in the ACTRIS air standards should be elucidated.

For m/z 79 (benzene) the difference to the assigned values may also be explained by co-detection of compounds. For m/z 93 (toluene + *p*-cymene) WCC-VOC obviously overestimated the toluene target values. As *p*-cymene was present in both gas cylinders this was expected. For NMHC_N_2 the *p*-cymene value was known (1.07 $\pm$ 0.079 nmol/mol). As in m/z 93 both toluene and *p*-cymene were detected, the target mole fraction in NMHC_N_2 for m/z 93 was therefore 2.29 nmol/mol. This target mole fraction of m/z 93 was almost perfectly matched by WCC-VOC with a measured value of 2.27 nmol/mol. This highlights the weakness of the PTR-MS method; it does not detect changes in the chemical composition of the gas sample. Thus the PTR-MS was a method for monitoring changes in the concentrations of a known matrix, but not for the identification of the compounds. The reported value for m/z 93 from SMR-II when referenced to the sum of toluene and *p*-cymene in NHMC_N_2 underestimated the target by about 30%. The same bias is observed when comparing the SMR-II data for other m/z and other samples to values reported by WCC-VOC. These results may likely be traced back to uncertainties in the calibration process and changes in the gas sample composition.

When applying calibration factors for specific compounds gained for dry gas samples to ambient measurement conditions it has to be considered that humidity in the gas sample may influence the instrument response. As some water gets from the ion source to the reaction chamber, as well as from the sample air, water clusters $H_3O^+(H_2O)$ are always present in the reaction chamber. The drift tube ion chemistry includes ionization of the measured compounds as well as formation of water clusters, which are ionized, too. Since there is also some back drift of sample air into the ion source, the abundance of primary ions is also influenced by the air sample, e.g. amount of water vapor (Tani et al., 2003) and oxygen (Ennis et al., 2005). Many compounds have high enough water affinity to be protonated in the collision with the water cluster as well as with protonated water. Additionally, changes in relative humidity do affect the measured signals. However benzene and toluene do not react with water cluster and thus their signals are humidity dependent. The highest signals for benzene and toluene have been measured when the relative humidity was low (20%) and the signals were decreasing with decreasing relative humidity (Warneke et al., 2001).

3.3 Conclusion

While PTR-MS is a real-time, on-line method that is less labor intense than the GC-MS methods for monitoring changes in mole fractions, another method is needed for determining the chemical composition of the gas samples. For correctly assigning amount fractions with PTR-MS analysis to specific compounds, the composition of the gas matrix needs to be considered as well as cluster formation and compound fragmentation. In addition, standards used for calibration should be traceable to a common scale and if diluted standards are used, the error in the dilution ratio must be as small as possible to minimize the bias to target amount fractions.

4. References

Barlow, R.: Statistics : a guide to the use of statistical methods in the physical sciences, Wiley, Chichester, 1989.

Blake, R. S., Monks, P. S., and Ellis, A. M.: Proton-Transfer Reaction Mass Spectrometry, Chem. Rev., 109, 861–896, 2009.

Bronštejn, I. N.: Handbook of mathematics, Berlin : Springer, Berlin, 2007.

De Gouw, J. and Warneke, C.: Measurements of volatile organic compounds in the earth's atmosphere using proton-transfer-reaction mass spectrometry, Mass Spectrom Rev, 26, 223-257, 2007.

De Gouw, J., Warneke, C., Karl, T., Eerdekens, G., Van der Veen, C., and Fall, R.: Sensitivity and specificity of atmospheric trace gas detection by proton-transfer-reaction mass spectrometry, Int. J. Mass Spectrom., 223-224, 365-382, 2003a.

de Gouw, J. A., Goldan, P. D., Warneke, C., Kuster, W. C., Roberts, J. M., Marchewka, M., Bertman, S. B., Pszenny, A. A. P., and Keene, W. C.: Validation of proton transfer reaction-mass spectrometry (PTR-MS) measurements of gas-phase organic compounds in the atmosphere during the New England Air Quality Study (NEAQS) in 2002, Journal of Geophysical Research D: Atmospheres, 108, ACH 10-11 - ACH 10-18, 2003b.

Ennis, C. J., Reynolds, J. C., Keely, B. J., and Carpenter, L. J.: A hollow cathode proton transfer reaction time of flight mass spectrometer, Int. J. Mass Spectrom., 247, 72-80, 2005.

Lindinger, W., Hansel, A., and Jordan, A.: On-line monitoring of volatile organic compounds at pptv levels by means of Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) Medical applications, food control and environmental research, Int. J. Mass Spectrom. Ion Proces., 173, 191-241, 1998.

Taipale, R., Ruuskanen, T. M., Rinne, J., Kajos, M. K., Hakola, H., Pohja, T., and Kulmala, M.: Technical note: Quantitative long-term measurements of VOC concentrations by PTR-MS - Measurement, calibration, and volume mixing ratio calculation methods, Atmospheric Chemistry and Physics, 8, 6681-6698, 2008.

Tani, A., Hayward, S., and Hewitt, C. N.: Measurement of monoterpenes and related compounds by proton transfer reaction-mass spectrometry (PTR-MS), Int. J. Mass Spectrom., 223-224, 561-578, 2003.

Warneke, C., De Gouw, J. A., Kuster, W. C., Goldan, P. D., and Fall, R.: Validation of atmospheric VOC measurements by proton-transfer-reaction mass spectrometry using a gas-chromatographic preseparation method, Environmental Science and Technology, 37, 2494-2501, 2003.

Warneke, C., Van Der Veen, C., Luxembourg, S., De Gouw, J. A., and Kok, A.: Measurements of benzene and toluene in ambient air using proton-transfer-reaction mass spectrometry: Calibration, humidity dependence, and field intercomparison, Int. J. Mass Spectrom., 207, 167-182, 2001.

5. Tables

Table S1: Participants of the ACTRIS NMHC intercomparison listed by institution and site (with acronym). For monitoring networks, it is differentiated between GAW and EMEP (VOC) and their status in the respective network is listed.

Institution	Site	Acronym	Monitoring networks	
			GAW	EMEP (VOC)
Czech Hydrometeorological Institute (Czech Republic)	Kosetice	KOS	regional	x
Finnish Meteorological Institute (Finland) [a]	Pallas	PAL	global	-
	SMEAR II, Hyytiälä	SMR	regional	-
University of Helsinki (Finland)	SMEAR II, Hyytiälä	SMR II	regional	x
Ecole des Mines de Douai (France)	Mines des Douai	DOU	regional*	x
National center for scientific research, Gif-sur-Yvette Cedex (France) [b]	Sirta	SIR	-	-
National center for scientific research, Aubière Cedex (France)	Puy-de-Dôme	PUY	regional*	-
German Weather Service (DWD), Hohenpeissenberg (Germany)	Hohenpeissenberg	HPB	global	-
Research Center Jülich (Germany) [b]	Jülich	FZJ	-	-
Technische Universität München (Germany)	Zugspitze-Schneefernerhaus	ZSF	global	-
Karlsruhe Institute of Technology, Garmisch-Partenkirchen (Germany)	Garmisch-Partenkirchen	WCC-VOC	WCC	-
Umweltbundesamt Station Schmücke (Germany)	Schmücke	SMK	contributing	x
University of Urbino (Italy)	Monte Cimone	CMN	global	-
European Commission Joint Research Centre, Ispra (Italy)	Ispra	IPR	regional	x
National University of Ireland/ University of Bristol (United Kingdom)	Mace Head	MHD	global	-
Norwegian Institute for Air Research, Kjeller (Norway) [b]	NILU	NILU	-	-
Swiss Federal Laboratories for Materials Science and Technology (Empa),	Rigi	RIG	regional	x

Dübendorf (Switzerland) [a]	Jungfraujoch	JFJ	global	-
Ricardo-AEA, Harwell/Centre for Ecology & Hydrology (United Kingdom) [a]	Auchencorth	AUC	regional	x
	Harwell	HAR	contributing	x
National Centre for Atmospheric Science, University of York (United Kingdom)	York	YRK	global	-

290 WCC: World Calibration Centre; * in progress, stations are assessed for GAW regional

291 [a] institutes where two instruments took part in the intercomparison. [b] participating neither in GAW nor in EMEP networks

Table S2a: Analysis methods used in the ACTRIS NMHC intercomparison exercise (stations acronym, instrument, ozone (O_3) trap, water (H_2O) trap, preconcentration unit, sample volume, trap adsorbents, re-focus/cryofocus). For acronyms see Table S1.

Acronym	Instrument	O_3 trap	H_2O trap	Preconcentration unit	Sample volume [ml]	Adsorbents and adsorption (ads.) and desorption (des.) temperatures	Re-focus/cryofocus and temperatures
GC-FIDs							
PerkinElmer systems with Deans switch							
AUC	PerkinElmer GC-FID/FID	no	Nafion®-Dryer	PerkinElmer Turbomatrix with online accessory[a]	600	Air Toxics Analyser Trap[b] (ads. at -30°C, des. at 320°C)	no
HAR	PerkinElmer GC-FID/FID	no	Nafion®-Dryer	PerkinElmer Turbomatrix with online accessory[a]	600	Air Toxics Analyser Trap[b] (ads. at -30°C, des. at 320°C)	no
PAL	PerkinElmer GC-FID/FID	no	Nafion®-Dryer	PerkinElmer Turbomatrix 300 with online accessory[a]	1200	Air Toxics Analyser Trap[b], mixed bed carbon (ads. at -40°C, des. at 325°C)	no
SMK	PerkinElmer GC-FID/FID	no	Nafion®-Dryer	PerkinElmer Turbomatrix 300 with online accessory[a]	500	TD/ATD Air Monitoring Trap (ads. at -30°C, des. at 325°C)	no
Other systems with Deans switch							
IPR	Agilent GC-FID/FID	no	Nafion®-Dryer	PerkinElmer Turbomatrix with online accessory[a]	1360	Air Toxics Analyser Trap[b] (ads. at -30°C, des. at 380°C)	no
KOS_A	Agilent 7890 GC-FID/FID	no	Nafion®-Dryer	Markes UNITY-Thermal Desorber	400	Air Toxics Analyser Trap[b] (ads. at -20°C, des. at 310°C)	no
DOU	Chrompak GC-FID/FID	no	Nafion®-Dryer	Entech	360	glass beads (ads. at -120°C, des. at 70°C)	glass beads, Tenax® (-50°C to 220°C)
YRK	PerkinElmer GC-FID/FID	no	Glass volume at -27°C	custom made (OPTIC PTV injector housed in a custom made cooling block)	1000	Carbopack® B, Carboxen® 1000 (ads. at -20°C, des. at 350°C)	no
Two column systems with split injection							
WCC-VOC	Varian 3800 GC-FID/FID	no	Silcosteel® at -30°C	custom made	400	Carbopack® BHT (ads. at -120°C, des. at 200°C)	no

One column system							
RIG	Agilent GC-FID	no	Nafion®-Dryer	custom-made (Adsorption Desorption Unit)	600	Stainless steel tube with fused silica beads, Carboxen® 1003, Carboxen® 1016, Carbosieve® S-III (ads. at -45°C, des. at 235°C)	no
HPB_A	Varian 3800 GC-FID	YES but not used in this exercise	1/8" sulfinert U-tube (Restek) at -40°C	custom-made	750	glass beads (ads. at -180°C, des. at 300°C)	no
HPB_B (FID)	Agilent 6890 GC-FID/MS	YES but not used in this exercise	no	custom-made	400 (for nitrogen); 1500 (ambient air)	fritted glass tube with Tenax® TA, Carbopack® X, Carboxen® 569 (ads. at 30°C, des. at 200°C)	Cryofocus on methyl silicone capillary at -180°, des. at 60°C
FZJ_B	Agilent 6890 GC-FID	if necessary O_3 was removed by a SS capillary heated to 120°C prior to sampling in the canister		custom-made (valve unit and cryotrap)	800	glass beads (ads. at -180°C des. at 130°C)	partly re-focussing on column-head at -60°C
KOS_B	Agilent 6890 GC-FID	no	Nafion®-Dryer	Markes UNITY-Thermal Desorber	400	Air Toxics Analyser Trap[b] (ads. at -20°C, des. at 310°C)	no
GC-MSs							
CMN	Agilent GC-MS	no	Nafion®-Dryer	Markes UNITY-Thermal Desorber	1000	Carbograph® 1, Carboxen® 1003, Carbosieve® SIII (ads. at -30°C, des. at 310°C)	no
FZJ_A	Custom-made GC with 5975C inert MSD	42.5 cm Silcosteel®, 0.25 mm i.d., 120 °C	no	custom-made (Gerstel)	150	Glas liner with Carbotrap® C, Carbotrap® B, Carbosieve®SIII (adsorption at 30°C, desorption at 225°C)	focus trap (Carbopack® X) (adsorption at 35°C, desorption at 225°C)
HPB_B (MS)	Agilent 6890 GC-FID/MS	YES but not used in this exercise	no	custom-made	400 (for nitrogen); 1500 (ambient air)	fritted glass tube with Tenax® TA, Carbopack® X, Carboxen® 569 (ads. at 30°C, des. at 200°C)	cryofocus on methyl silicone capillary at -180° to 60°C
PUY	PerkinElmer GC-MS	no	no	PerkinElmer ATD	800 and 1500	Tenax® TA, Carbosieve® S-III (ads. at 20°C, des. at 280°C)	Tenax® TA, Carbosieve®

							(adsorption at -10°C, desorption at 280°C)
SIR	Varian 3800 GC-MS (ion trap)	no	no	PerkinElmer Turbomatrix	700	Tenax® TA (ads. at room temperature, des. at 225°C)	cold trap with Air Toxics (Carbosieve® SIII, Carpopack® B), (adsorption at 0°C, desorption at 325°C)
SMR	Agilent GC-MS	no	no	Markes UNITY-Thermal Desorber	1800	Tenax® TA, Carbopack® B, molecular sieve (ads. at 25°C, des. at 300°C)	no
Medusa systems							
JFJ	Agilent GC-MS	no	2x Nafion®-Dryer	custom-made	2000	HaySepD® (ads. at -160°C, des. at 100°C)	cryofocussing on second trap with HaySepD® (adsorption at -160°C, desorption at 100°C)
MHD	Agilent GC-MS	no	2x Nafion®-Dryer	custom-made	2000	HaySepD® (ads. at -165°C, des. at 100°C)	cryofocussing on second trap with HaySepD® (adsorption at -165°C, desorption at 100°C)
NILU	Agilent GC-MS	no	2x Nafion®-Dryer	custom-made	2000	HaySepD® (ads. at -165°C, des. at 100°C)	cryofocussing on second trap with HaysepD® (adsorption at -165°C, desorption at 100°C)
PTR-MS							
SMR II	Ionicon Analytik	no	no	no	continuous flow 0.1 l/min	no	no
WCC-VOC	Ionicon Analytik	no	no	no	continuous flow 0.1 l/min	no	no

SS = stainless steel

[a] standard online accessory (see PerkinElmer http:// www.perkinelmer.co.uk/content/applicationnotes/app_gaschromaozoneprecursoranalysis.pdf) including unheated SS lines and valves

[b] Carbopack® B, Carbosieve® SIII are the adsorbents of the Air Toxics Analyser Trap (personal communication: M. Dinse (PerkinElmer))

296 Table S2b: Analysis methods used in the ACTRIS intercomparison exercise (stations acronym, pre-column, column, column temperature, sample path, injector type,
297 and calibration gas). For acronyms see Table S1. All instruments used helium as carrier gas.

Acronym	Pre-column (length x inner diameter x film thickness)	Column (length x inner diameter x film thickness)	Column temperature	Sample path	Injection type	Laboratory standard (manufacturing year of standard)
GC-FIDs						
PerkinElmer systems with Deans switch						
AUC	no	SGE BP-1 (50 m x 0.22 mm x 1 µm), Al_2O_3/Na_2SO_4 PLOT (50 m x 0.32 mm), Deans switch	45°C for 15 min, 5°C/min to 170°C, 15°C/min to 200°C, hold for 6 min	SS not heated	outlet split, when trap is heated, set to 2 ml/min, split ratio ~1:1	30 NMHCs, 4 nmol/mol, NPL (2007)
HAR	no	SGE BP-1 (50 m x 0.22 mm x 1 µm), Al_2O_3/NA_2SO_4 PLOT (50 m x 0.32 mm), Deans switch	45°C for 15 min, 5°C/min to 170°C, 15°C/min to 200°C, hold for 6 min	SS not heated	outlet split, when trap is heated, set to 2 ml/min, split ratio ~1:1	30 NMHCs, 4 nmol/mol, NPL (2009)
PAL	no	SGE BP-1 (50 m x 0.22 mm x 1 µm), Agilent GS- Al_2O_3/Na_2SO_4 PLOT (50 m x 0.32 mm), Deans switch	46°C for 15 min, 5°C/min to 170°C, 15°C/min to 200°C	SS	split injection	30 NMHCs, 4 nmol/mol, NPL (2011)
SMK	no	SGE BP-1 (50 m x 0.22 mm x 1.0 µm), Al_2O_3/NA_2SO_4 PLOT (50 m x 0.32 mm x 5µm), Deans switch	46°C for 15 min, 5°C/min to 170°C, 15°C/min to 200°, hold until 50 min	SS	outlet split, when trap is heated, set to 2 ml/min, split ratio ~1:1	30 NMHCs, 4 nmol/mol, NPL (2012)
ZSF	no	SGE BP-1 (50 m x 0.22 mm x 1µm)Varian Al_2O_3/Na_2SO_4 PLOT (50 m x 0.32 mm x 5 µm), Deans switch	46°C for 15 min, 5°C/min to 170°C, 15°C/min to 200°C, hold for 8 min	SS (transfer line at 230°C)	outlet split, when trap is heated, set to 2 ml/min, split ratio ~1:1	30 NMHCs, 4 nmol/mol, NPL (2010)
other systems with Deans switch						
IPR	no	J&W DB-1 (50 m x 0.318 mm x 1.20 µm), HP- Al_2O_3/KCl PLOT (50 m x 0.321 mm x 8 µm), Deans switch	40°C for 5 min, 6°C/min to 200°C, hold for 15 min	teflon at room temperature, SS and Silcosteel® at 250°C	outlet split, when trap is heated, set to 2 ml/min, split ratio ~1:1 (controlled with needle valve)	30 NMHCs, 4 nmol/mol, NPL (2011)
KOS_A	no	Varian CP Al_2O_3/Na_2SO_4 PLOT	45°C for 5 min, 6°C/min to 160°C,	SS not heated (transfer line	split, trap flow 40 ml/min,	30 NMHCs,

		(50 m x 0.32 mm), J&W DB-1 (50 m x 0.32 mm), Deans switch	9°C/min to 200°C, hold for 14 min	>200°C)	split 20 ml/min	10 nmol/mol, NPL (2010)
DOU	no	Varian CP Sil-5 CB (50 m x 0.32 mm 1.2 µm), Al_2O_3/KCl PLOT (50 m x 0,25 mm x 1 µm), Deans switch	35°C for 10 min, 7.5°C/min to 200°C, hold for 15 mins	SS heated and Silcosteel®	split less	33 NMHCs, 2 nmol/mol, NPL (2012)
YRK	no	Varian Al_2O_3/KCl PLOT (50 m x 0.53 mm), 2x Chromopack-LOWOX (each 10 m x 0.53 mm x 10 µm)	40°C for 15.5 min, 13°C/min to 110°C, 8°C/min to 200°C	SS heated	split 70% PLOT/ 30% LOWOX	30 NMHCs, 4 nmol/mol, NPL (2011)
Two column system with split injection						
WCC-VOC	no	Varian CP-Silica PLOT (30 m x 0.32 mm x 4 µm),Varian VF 1 MS (60 m x 0.25 mm x 1 µm), parallel	-30°C for 8.7 min, 40°C/min to 20°C, 5°C/min to 120°C, 20°C/min to 220°C, 43°C/min to 40°C	Silcosteel®, sulfinert at room temperature, SS at 100°C	split on two parallel columns 1:1 (flow restrictor)	26 NMHCs, 1.3 nmol/mol, NPL (2011)
One column systems						
RIG	no	Varian Al_2O_3/KCl PLOT (50 m x 0.53 mm)	37°C for 11 min, 6.5°C/min to 180°C, 10°C/min to 200°C, hold for 9.5min, 50°C/min to 210°C, hold for 20 min	SS not heated	splitless	30 NMHCs, 4 nmol/mol, NPL (2008)
HPB_A	no	Varian Al_2O_3/KCl PLOT (50 m x 0.53 mm)	40°C for 2 min, 4°C/min to 72°C, 6°C/min to 200°C, isothermal at 200° for 33.67 min	Silcosteel® at room temperature and 120°C; SS at 150°C	splitless	30 NMHCs, 2 nmol/mol, NPL (2009)
HPB_B (FID)	no	SGE BPX-5 (50 m x 0.22 mm x 1 µm)	10°C for 5 min, 6°C/min to 240°C	Silcosteel®, ultimetal at room temperature or at 150°C; SS and VALCO valves at 150°C	splitless, column outflow is split 1:1,5 to MS:FID	30 NMHCs, 2 nmol/mol, NPL (2009)
FZJ_B	no	Agilent DB-1 (120 m x 320 µm x 3µm)	-60°C for 8 min, 4°C/min to 180°C, 20°C/min to 220°C, isothermal at 220°C for 10 min	SS silanised, ACTRIS samples additionally 75 cm PFA-tubing	splitless	74 VOCs, 0.16-10.8 nmol/mol, Apel-Riemer Environmental, Inc. 54 VOCs, 0.16-10.8 nmol/mol, Apel-Riemer

						Environmental, Inc. (2009)
KOS_B	no	J&W DB-1 (50 m x 0.32 mm)	45°C for 5 min, 6°C/min to 160°C, 9°C/min to 200°C, hold for 14 min	SS not heated (transfer line >200°C)	splitless	30 NMHCs, 10 nmol/mol, NPL (2010)
GC-MSs						
CMN	no	J&W GasPro PLOT (30 m x 0.35 mm)	49°C for 6 min, 9.5°C/min to 145°C, hold for 2 min, 10°C/min to 250°C, hold for 20 min	SS (working std); Silcosteel® (NPL) and PTFE	splitless	30 NMHCs, 4 nmol/mol, NPL (2012)
FZJ_A	no	Agilent DB 624 (20 m x 0.18 mm)	35°C for 0.3 min, 120°C/min to 220°C, isothermal at 220°C for 1.46 min	PFA tubing and Silcosteel® tubing (Restek), valve sealing (Valcon E rotor material by VICI, 493 K); GERSTEL Graphpack fittings, Silcosteel® liner with adsorption material	splitless	74 VOCs, 0.16-10.8 nmol/mol, Apel-Riemer Environmental, Inc. 54 VOCs, 0.16-10.8 nmol/mol, Apel-Riemer Environmental, Inc. (2009)
HPB_B (MS)	no	SGE BPX-5 (50 m x 0.22 mm x 1 µm)	10°C for 5 min, 6°C/min to 240°C	Silcosteel®, sulfinert, ultimetal at room temperature or at 150°C. SS, VALCO valves at 150°C	splitless, column outflow is split 1:1,5 to MS:FID	30 NMHCs, 2 nmol/mol, NPL (2009)
PUY	no	OPTIMA-5MS (60 m x 0.25 mm, 0.25 µm)	35°C for 5 min, 5°C/min to 250°C, hold 2 min	SS not heated	outlet split: 30 mL/min, 1.5 mL/min on column; inlet split: 50 mL/min, 20 mL/min on trap	29 NMHCs, 1-10 nmol/mol, Air Products (2007), 2 nmol/mol, Restek
SIR	no	CP PoraBOND Q (25 m x 0.25 mm x 3.00 µm)	100°C to 250°C (Run time: 30 min)	SS and fused silica at 220°C	split 1/5 between preconcentration unit and column (5 mL/min, 1.4 mL/min on column)	30 NMHCs, 4 nmol/mol, NPL (2010)

SMR	no	Agilent DB-5 (60 m x 0.235 mm x 1 um)	50°C, 4°C/min to 150°C, 8°C/min to 290°C	For this excercise: Silcosteel® lines	splitless	7 NMHCs, 2 nmol/mol, NPL (2011)
Medusa systems						
JFJ	no	Varian CP 7351 CP- CP PoraBOND Q (25 m x 0.32 mm x 5 µm)	40°C for 16.6 min, 23°C/min for 7 min, 200°C for 6.6 min	SS 40°C	splitless	30 NMHCs, 4 nmol/mol, NPL (2008)
MHD	MS-4 Å and HiSiv-3000 in 80 cm x 0.75 mm SS (Restek)	Varian CP 7351 CP- CP PoraBOND Q (25 m x 0.32 mm x 5 µm)	40°C, 10°C/min to 200°C	SS	splitless	45 VOCs, 0.4-1.3 nmol/mol, Apel-Riemer Environmental Inc. (2006)
NILU	Molecular sieve 4 Å, mesh HISIV-3000 at 40°C	Varian CP PoraBOND Q (25 m x 0.32 mm x 5 µm)	40°C, 22.9°C/min to 200°C, 40°C	SS, PEEK, KNF pump (neoprene diaphragm), flowmeter, pressure gauge	splitless	30 NMHCs, 2.7 nmol/mol, NPL (2012)
PTR-MS						
SMR II	no	no	no	no	no	16 VOCs, 0.84-1.14 nmol/mol, Apel-Riemer Environmental, Inc.
WCC-VOC	no	no	no	no	no	3 different NPL calibration standards

SS = stainless steel, NPL = National Physical Laboratory, UK

298

299

Table S3: Overview of NMHC measurement performance in NMHC_N_2: relative difference [%] between measured value and assigned value (positive value: higher value than assigned; negative value: lower value than assigned). Colour code: green (DQOs 1): value within the 5%-class (ACTRIS DQO, Table 2 and Equation 1 main paper); blue (DQQs 2): value within the 10%-class (former GAW DQO); red (DQOs 3): value outside the 10%-class. White numerics: reported uncertainty combined with the uncertainty of the reference value covers the observed deviation. Black numerics: reported uncertainty is underestimated. N (compounds) indicates the number of compounds reported by the respective station; N (stations) indicates the number of stations reporting the respective compound. Please note that HPB and Empa assigned mole fractions to NMHC_N_2.

	instrument	station/compounds	ethane	propane	n-butane	2-methylpropane	n-pentane	2-methylbutane	n-hexnane	2-methylpentane	n-heptane	n-octane	2,2,4-trimethylpentane	ethene	propene	1-butene	trans-2-butene	cis-2-butene	1,3-butadiene	1-pentene	trans-2-pentene	isoprene	ethyne	benzene	toluene	ethylbenzene	*m,p*-xylene	*o*-xylene	N (compounds)	DQOs 1	DQOs 2	DQOs 3
GC-FID-FID		AUC	4.1	-4.4	-45.2	-6.3	-30.1	-29.7	-2.9	-4.8	-3.9	-1.3	-2.2	3.5	-13.1	-11.2	2.8	-6.2	-9.8	-9.4	-6.0	-4.8	-4.0	-2.3	-4.5	0.9	0.0	-2.3	26	16	7	3
		HAR	-2.0	-1.4	-0.5	-3.8	-2.3	-2.7	-2.9	-4.6	-2.4	-3.7	-1.4	-0.9	-4.2	-0.6	0.0	-2.3	-2.5	-4.5	-3.7	-1.6	-4.2	-3.0	-9.4	-20.5	-20.8	-21.7	26	22	1	3
	Deans switch PE	PAL	1.3	-4.4	-4.0	-3.0	-1.9	-2.2	-5.2	-5.8	-5.6	-3.2	-10.6	-16.0	-5.8	-11.8	-5.9	-4.8	-8.4	-4.1	-1.4	-2.2	-2.1	-7.2	-5.2	-7.0	-7.2	-5.6	26	14	11	1
		SMK	-5.7	-3.8	-6.0	-5.2	-6.1	-5.3	-7.0	-10.6	-6.3			-6.6	-2.5	-7.1	-6.5	-7.3	-5.1	-7.1	-5.3	-6.2	-6.2	-6.0	8.7	2.5	4.3	6.5	24	5	18	1
		ZSF	-3.8	1.5	-17.3	-13.6	-32.1	-17.6	-8.9	-11.8	-2.7		-3.6	-16.8	27.4	-21.7	-20.1	-19.1	-17.1	-26.4	-19.6	-17.0	-21.8	-28.9	-0.8	-1.4	-3.9	-0.7	25	8	6	11
		IPR	-0.1	-4.6	-4.7	-4.2	-2.4	-3.1	-3.4	-2.6	-2.3	-2.7	-2.7	23.8	-4.8	-1.7	-5.0	-3.2	-3.2	-4.5	-4.0	-2.8	95.1	-4.9	-6.4	-8.4	-10.6	-9.3	26	19	5	2
	Deans switch	KOS_A	-4.3	5.5	6.3	2.9	1.9	1.9	1.8	1.0	1.1	3.1	0.1	-70.5	-1.6	-6.4	-8.6	-11.3	-2.9	-1.9	1.7	5.6	-4.3	2.8	4.5	-3.6	-6.2	-3.0	26	19	6	1
		DOU	-0.1	-1.2	-1.4	-0.8	-1.6	0.6	-7.2	-4.1	-4.9	-7.4	-4.3	-3.1	0.2	0.1	-0.2	-1.3	1.2	0.1	-0.4	-0.4	-6.9	-5.1	-9.1	-9.5	-9.5	-8.1	26	20	6	0
	2 columns, split	YRK	-3.4	-1.9	-1.3	-0.8	-0.8	-0.3	-1.4	-1.9	-2.0	-2.0	-1.6	-4.3	-0.6	-0.9	-1.5	-1.7	-0.8	-0.9	-1.6	0.1	1.2	-1.4	-2.9	3.9	2.4	-3.9	26	26	0	0
GC-FID		RIG	-5.3	-5.7	-2.0	-2.5	-0.8	-0.4	-7.2	-6.4	-5.5			-4.4	-1.2	-0.1	0.1	-0.6	0.7	-2.0	-1.9	-3.4	-1.7	-2.3	-3.9	1.2	-8.4	-7.9	24	18	6	0
		HPB_A	0.3	1.3	-0.5	-0.7	-0.5	0.4	1.5	0.1	-2.1	0.4	-0.5	-1.1	0.5	-1.0	-1.2	0.1	0.3	-3.2	-0.6	-2.2	-13.6	-0.9	-2.5	-2.8	-7.3	-2.5	26	24	2	0
	1 column	HPB_B (FID)			-1.9	-1.3	-3.1	-1.2	-2.2	-2.2	-3.6	-2.0	-3.6			0.8	-4.0	-1.4	-6.2	-4.4	3.5	-15.5		-2.0	-3.7	-5.2	-8.6	-2.9	21	18	3	0
		FJZ_B	-18.7	-16.1	8.2	-9.8	-1.2	-9.9	-10.2	-10.0	-13.9	-3.3		-10.4	-31.9	-17.7	-23.2	-13.4	-33.5	-14.7	-14.1	-14.0	-45.7	-9.8	-5.7	-8.1	-4.6	-10.4	25	4	13	8
		KOS_B																						-3.8	-5.2	-8.4	-10.8	-7.6	5	3	2	0
GC-MS		CMN		1.9	13.0	9.1	0.6	21.6	387	145	90.1	42.6	64.3		13.3	-6.1	20.0	-19.7	-20.1				1.5	-3.2	-13.7	-7.1	-5.7	-28.6	21	5	7	9
		FJZ_A			121.2	60.6	1.2	5.7	0.0	-66.8	4.5	-3.0				-51.0	-14.6	7.5	7.9	-3.7	35.5	-2.5		2.9	-11.0	-2.7	-29.9	-9.6	20	8	6	6
		HPB_B (MS)			-4.9	-0.8	-1.0	-0.4	-1.7	-2.9	-3.2	-2.1	-1.3			-3.3	-2.5	-1.9	-3.9	-5.0	-2.0	-3.0		0.8	1.8	-1.1	-4.0	-0.1	21	21	0	0
		PUY							4.5		9.3	4.5										4.0			1.6	1.2	-5.8	51.8	8	6	1	1
		SIR							-6.4		0.4	7.3										-18.6		-2.1	1.1	6.2	9.4	9.4	9	3	6	0
		SMR																				36.6		-13.7	-13.2	-14.9	-17.9	-13.2	6	0	4	2
		JFJ	-2.4	1.8	17.9	12.0	8.5	14.9																2.9					7	3	1	3
	Medusa	MHD	4.4	1.2	9.3		13.6	8.5																					5	2	2	1
		NILU	1.7	3.1	6.9	4.7	7.4	4.4						2.8	5.1								0.3						9	6	3	0
		N (stations)	15	16	19	18	19	19	18	16	18	15	12	13	14	16	16	16	16	15	15	18	14	20	20	20	20	20				
		DQOs 1	12	13	8	11	13	11	10	9	12	12	10	7	9	8	9	9	9	10	10	11	8	15	14	11	9	14				
		DQOs 2	2	2	6	4	3	4	6	3	4	2	0	4	3	6	5	7	5	4	4	6	3	4	6	8	8	3				
		DQOs 3	1	1	4	2	3	4	2	4	2	1	2	2	2	2	2	0	2	1	1	1	3	1	0	1	3	3				

PE: PerkinElmer

Table S4: Overview of NMHC measurement performance in NMHC_air: relative difference [%] between measured and assigned values (positive value: higher value than assigned; negative value: lower value than assigned). For compounds < 0.1 nmol/mol the values are given in pmol/mol. They are indicating the difference to the assigned values. Colour code: green (DQOs 1): value within the 5%-class (ACTRIS DQO, Table 2 and Equation 1 main paper); blue (DQQs 2): value within the 10%-class (former GAW DQO); red (DQOs 3): value outside the 10%-class. White numerics: reported uncertainty combined with the uncertainty of the reference value covers the observed deviation. Black numerics: reported uncertainty is underestimated. N (stations) indicates the number of stations reporting the respective compound. *: mole fractions < 0.1 nmol/mol. Please note that HPB and Empa assigned mole fractions to NMHC_air.

	alkanes															alkenes										alkynes		aromatics							
station/compounds	ethane	propane	n-butane	2-methylpropane	n-pentane	2-methylbutane	n-hexnane	2-methylpentane	3-methylpentane	2,2-dimethylbutane	2,3-dimethylbutane *	cyclohexane	n-heptane	n-octane *	2,2,4-trimethylpentane	ethene	propene	1-butene	2-methylpropene	trans-2-butene *	cis-2-butene *	1,3-butadiene *	1-pentene *	trans-2-pentene *	cis-pentene *	2-methyl-2-butene	isoprene *	ethyne	propyne *	benzene	toluene	ethylbenzene	*m,p* -xylene	*o* -xylene	N (compounds)	N (compounds considered)	DQOs 1	DQOs 2	DQOs3
AUC	2.7	-2.1	-38.6	-10.4	-31.5	-34.2	-9.6	-27.4					-0.9	17	37.9	-16.7	12.1	-36.8		-10	16	-21	1	-9			-2	-13.9		-7.6	-0.1	7.3	1.0	26.5	26	21	7	8	6
HAR	-5.2	0.5	-6.0	-6.0	-5.0	-8.0	0.6	-15.5					0.7	54	82.1	-4.9	1.2	16.7		31	0	12	3	13			6	-9.5		6.5	-2.8	-14.6	-19.8	-5.7	26	21	12	7	2
PAL	-1.1	1.0	-3.7	-3.5	-0.4	-0.1	-8.6	-6.0					-6.9	0	29.2	-4.0	-9.6			28	-4		11	15			5	-6.1		-10.0	2.1	-15.0	-4.3	-2.8	24	20	13	7	0
SMK	-1.2	-6.5	-8.6	-10.1	-7.2	-7.1	-11.1	24.4					-6.3			-5.0	11.0	-0.6		-13	-16	-26	12	5			-12	3.5		-12.8	9.2	8.3	10.3	27.1	24	21	5	13	3
ZSF	2.8	2.8	-19.8	-18.7	-29.7	-13.0	8.6	-18.7					2.6		42.4	-5.4	-6.3	15.6		-30	-36	38	-9	-9			0	-10.2		-9.0	11.3	37.7	12.6	15.6	25	21	4	9	8
IPR	-2.4	-2.5	-1.6	-5.6	-0.7	-0.7	13.7	-0.5					-31.9	0	200	23.1	-6.7	-11.5		3	-15	-11	-3	7				50.3		-8.4	4.3	-14.0	-3.4	10.7	25	20	10	6	4
KOS_A	21.8	1.2	-1.1	-0.8	-0.8	-0.4	0.0	-3.7					-2.2	-2	5.6	-56.8	-10.7	-37.6		-16	-23	-10	3	7			-5	-32.5		-1.5	2.8	-4.0	-4.6	30.9	26	21	14	2	5
DOU	-5.4	-2.5	-4.1	-5.5	-5.4	-3.3	1.9	2.6	40.0	54.1		9.3	-7.2		57.2	-6.2	-4.9	-16.7	-12.0	-10	-21	-15		2	-2		-2	-2.7	-15	-7.6	-3.6	0.0	-11.4	-3.6	30	25	16	6	3
YRK	-3.3	-1.6	-3.1	-5.0	-3.2	-2.2	0.0	53.6		39.7	26	1.4	-2.3	4	4.1	-10.5	-5.3	-1.8	-16.8	-6	-14	-16	11	0	4	-90.4	-5	-1.0	1	6.5	20.4	52.9	49.0	29.4	33	25	15	3	7
RIG	0.6	-0.4	-1.7	-4.0	-1.2	7.5	-6.4	22.7	0.5	37.4	-39	9.3	-18.1			-0.8	-0.5	-0.9	-28.1	24	-1	-6	8	10	0	6.4	5	1.1		-0.2	-6.6	17.1	1.1	5.4	31	26	17	5	4
HPB_A	0.2	-1.5	-1.5	0.3	-4.7	-1.0	29.8	-37.4	38.7	-7.0	-3	-8.5	0.6	-4	-4.2	0.4	0.2	-3.7	-4.0	-1	-1	-1	-1	-4	-2		-2	7.5	9	0.0	-3.4	2.8	0.7	2.1	33	25	19	3	3
FJZ_B	-5.7	-12.9	-19.9	-9.1	-2.2	8.3	-6.9	5.3	14.9	-3.3	36	-0.2	-10.0	-8		-32.1	-29.2							-15	-8	-13.9		-3.9		1.4	8.2	-15.3	-7.0	1.3	25	23	7	11	5
CMN		-12.4	5.3	58.8	-6.0	17.2	415	177					84.9	10	75.0		10.3	-33.9		36	650	-21						-21.2		0.4	-17.0	-10.5	-5.1	4.3	21	17	4	4	9
FJZ_A			30.3	64.9	-1.3	5.5	3.5	71.3					11.6	6				412		20	23	75	88	3			57			2.1	-11.5	-10.4	-30.6	-6.8	20	16	5	3	8
HPB_B (M					-0.6	0.3	0.0	-4.9					-2.8	3	5.6					1	-9	-5	9	20			-4			3.7	2.1	-2.4	-3.3	5.7	18	14	12	2	0
PUY							-26.1						1.1	-29													7				7.7	-9.7	-8.7	53.0	8	7	2	3	2
SIR							-2.5						13.1	9													-9			11.7	4.8	-10.1	-24.4	6.1	9	8	4	2	2
SMR																											-6			9.4	3.1	-2.4	-7.4	11.7	6	6	3	3	0
JFJ	1.7	2.6	16.6	7.2	10.2	6.7																								6.3					7	7	2	3	2
MHD	5.0	1.9	6.0		12.8	-4.2																													5	5	3	1	1
NILU	0.7	-1.7	3.1	-9.7	10.9	2.3										0.6	4.3											-8.0							9	9	6	2	1
N (station	15	16	17	16	18	18	17	15	4	5	4	5	17	13	11	13	14	12	4	14	14	13	12	14	5	3	15	14	3	18	18	18	18	18					
DQOs 1	13	13	8	7	10	9	7	6	1	1	0	2	8	0	0	6	6	0	0	0	4	10	0	5	4	1	14	5	0	7	10	5	8	10					
DQOs 2	1	1	4	5	3	6	5	0	0	1	0	3	4	0	0	4	7	0	0	0	5	1	0	9	1	1	0	6	0	11	6	10	6	3					
DQOs 3	1	2	5	4	5	3	5	9	3	3	0	0	5	0	0	3	1	0	0	0	5	2	0	0	0	1	1	3	0	0	2	3	4	5					

PE: PerkinElmer

Table S5: Repeatability in NMHC_N_2 [%]. Green colour indicates values within ACTRIS DQOs (DQOs 1, Table 2, main paper), blue values within GAW DQOs (DQOs 2), and red values outside GAW DQOs (DQOs 3).

		station/compounds	alkanes											alkenes									alkynes	aromatics								
			ethane	propane	*n*-butane	2-methylpropane	*n*-pentane	2-methylbutane	*n*-hexane	2-methylpentane	*n*-heptane	*n*-octane	2,2,4-trimethylpentane	ethene	propene	1-butene	*trans*-2-butene	*cis*-2-butene	1,3-butadiene	1-pentene	*trans*-2-pentene	isoprene	ethyne	benzene	toluene	ethylbenzene	*m,p*-xylene	*o*-xylene	N(compounds)	DQOs 1	DQOs 2	DQOs 3
GC-FID-FID		AUC	18.4	29.3	76.7	2.9	24.2	26.7	7.2	9.6	4.5	2.5	5.0	11.1	47.3	22.0	21.8	3.9	2.6	6.6	4.1	2.8	19.3	4.3	0.8	2.9	2.9	4.9	26	1	13	12
		HAR	4.6	1.8	6.1	2.3	0.8	7.1	2.3	2.2	2.4	2.4	2.6	2.2	6.6	1.7	2.1	3.1	3.8	6.5	1.7	2.4	6.8	3.0	3.9	3.6	3.9	1.7	26	5	18	3
	Deans switch PE	PAL	1.8	3.8	1.6	2.0	0.6	1.2	2.2	1.5	2.0	1.0	1.7	5.3	2.4	0.8	1.2	1.3	1.3	0.5	0.6	0.5	1.0	2.2	1.7	1.8	1.5	1.3	26	19	7	0
		SMK	2.0	3.6	1.1	2.4	0.6	0.8	1.4	1.7	1.5			3.6	4.1	2.8	0.7	1.0	0.8	1.2	1.0	0.6	9.3	1.5	5.0	0.4	1.9	0.6	24	16	7	1
		ZSF	0.2	1.2	1.6	1.3	1.9	2.0	1.0	0.5	1.2		1.3	2.1	1.2	2.5	1.7	0.2	0.9	0.6	1.9	0.6	1.4	1.8	1.3	1.5	0.4	2.3	25	22	3	0
		IPR	0.9	1.1	0.3	0.3	0.6	0.8	0.6	0.6	0.8	0.9	0.8	0.9	1.0	0.3	0.4	0.3	0.4	1.2	0.5	0.5	1.6	0.7	1.1	0.9	0.9	0.6	26	26	0	0
	Deans switch	KOS_A	1.1	1.9	1.3	0.4	0.3	0.4	0.6	0.3	0.6	0.7	0.1	3.3	0.5	0.7	0.7	0.5	2.0	0.3	0.3	0.6	1.9	0.3	1.1	0.4	1.2	0.4	26	25	1	0
		DOU	0.7	0.7	1.4	0.7	0.7	0.5	0.4	0.4	0.7	0.6	0.3	0.5	2.0	0.8	0.5	0.7	0.4	0.8	0.6	0.6	3.3	0.9	0.6	0.8	1.0	0.7	26	25	1	0
		YRK	0.9	0.2	0.1	0.2	0.3	0.2	0.1	0.2	0.2	0.4	0.2	0.5	0.2	0.1	0.2	0.2	0.1	0.2	0.2	0.3	0.6	0.4	0.9	1.1	0.5	0.7	26	26	0	0
GC-FID		RIG	0.8	1.4	2.0	1.1	1.6	0.8	2.8	2.3	1.4			1.9	1.0	1.0	0.7	0.2	0.6	1.3	1.1	1.9	1.7	3.2	4.3	9.0	10.3	15.1	24	17	5	2
		HPB_A	0.4	0.2	0.5	0.4	0.1	0.1	0.3	0.4	0.2	0.3	0.1	0.3	0.3	0.5	0.6	0.4	0.5	0.1	0.2	0.1	2.4	0.2	1.2	2.7	2.9	2.8	26	22	4	0
	1 column	HPB_B			0.9	0.3	0.3	0.2	0.4	0.4	0.4	0.2	0.1			0.5	0.6	0.3	1.5	0.4	0.5	1.8		0.2	0.1	0.2	0.3	0.2	21	21	0	0
		FZJ_B	4.5	2.9	2.5	0.5	1.1	0.5	1.0	1.0	1.9	1.9		3.6	7.4		0.9	1.4	9.7	7.1	2.1	2.5	11.8	3.2	2.2	2.3	2.5	2.8	24	9	14	1
		KOS_B																						1.0	1.6	1.7	2.2	4.1	5	3	2	0
GC-MS		CMN		2.1	2.2	0.3	2.7	6.6	7.8	11.6	8.8	8.1	9.9		9.1	10.9	3.6	9.0	9.7				0.3	2.7	3.3	5.6	4.0	4.3	21	2	13	6
		FZJ_A			10.8	7.3	1.8	1.5	1.2	1.1	1.3	2.5				6.9	1.2	1.9	6.5	0.8	1.2	0.9		1.2	0.5	2.0	1.2	0.9	20	14	4	2
		HPB_B_MS			1.1	0.7	0.4	0.8	0.4	0.7	0.7	0.3	0.5			0.9	0.8	0.5	0.5	0.4	1.2	0.5		1.3	1.2	1.2	1.1	1.0	21	21	0	0
		PUY							9.6		7.7	5.3										11.2			5.6	6.2	4.9	5.2	8	0	5	3
		SIR							2.7		3.2	2.3										4.0		1.4	2.7	2.7	1.2	0.9	9	3	6	0
		SMR																				1.9		1.8	1.8	1.7	1.6	1.6	6	6	0	0
		JFJ	0.4	0.5	0.4	0.3	1.0	0.8																0.1	0.4				8	8	0	0
	Medusa	MHD	0.3	0.3	0.3		0.4	0.7																					5	5	0	0
		NILU	0.2	0.1	0.1	0.4	0.3	0.6						0.3	0.2								0.3						9	9	0	0
		N (stations)	15	16	19	18	19	19	18	16	18	15	12	13	14	15	16	16	16	15	15	18	14	20	21	20	20	20				
		DQOs 1	11	11	14	13	17	16	11	12	12	9	9	6	9	10	13	13	11	12	13	13	8	14	14	10	11	11				
		DQOs 2	3	4	2	4	1	0	4	2	4	4	1	7	5	4	2	3	5	3	2	5	2	6	7	9	7	7				
		DQOs 3	1	1	3	1	1	3	2	2	2	2	2	0	1	1	1	0	0	0	0	0	4	0	0	1	2	2				

PE: PerkinElmer

Table S6: Repeatability in NMHC_air [%].For compounds with mole fractions < 0.1 nmol/mol the repeatability values are given in nmol/mol. Green colour indicates values within ACTRIS DQOs (DQOs 1), blue values within former GAW DQOs (DQOs 2), and red values outside former GAW DQOs (DQOs 3). * mole fractions < 0.1 nmol/mol.

			alkanes															alkenes										alkynes		aromatics								
	Instrument	station/compounds	ethane	propane	*n*-butane	2-methylpropane	*n*-pentane	2-methylbutane	*n*-hexane	2-methylpentane	3-methylpentane	2,2-dimethylbutane	2,3-dimethylbutane *	cyclohexane	*n*-heptane	*n*-octane *	2,2,4-trimethylpentane	ethene	propene	1-butene	2-methylpropene	*trans*-2-butene *	*cis*-2-butene *	1,3-butadiene *	1-pentene *	*trans*-2-pentene *	*cis*-pentene *	2-methyl-2-butene	isoprene *	ethyne	propyne *	benzene	toluene	ethylbenzene	*m,p*-xylene	*o*-xylene	N(compounds)	DQOs 1	DQOs 2	DQOs 3
GC-FID-FID		AUC	3.9	3.8	62.4	7.5	37.3	64.9	3.5	7.7					4.2	0.004	17.6	44.2	5.3	22.5		0.017	0.028	0.010	0.015	0.019			0.012	3.5		1.6	0.5	1.2	4.6	0.7	26	4	11	11
		HAR	2.0	3.3	1.3	2.2	2.1	3.1	8.5	0.4					3.0	0.030	4.1	1.3	4.3	8.8		0.009	0.008	0.007	0.005	0.005			0.007	3.6		11.2	0.5	6.1	6.6	4.8	26	5	18	3
	Deans switch PE	PAL	1.4	6.1	2.5	1.5	1.5	0.9	6.9	1.7					1.0	0.005	2.1	4.2	3.2	661.6		0.025	0.010	0.007	0.007	0.004	0.010		0.002	3.4		4.2	1.0	1.9	2.7	4.2	27	9	14	4
		SMK	4.2	7.4	1.6	1.6	2.1	1.2	3.5	1.3					3.1			2.3	1.7	4.0		0.002	0.003	0.003	0.004	0.002			0.002	1.4		1.1	1.0	4.6	1.6	2.3	24	12	11	1
		ZSF	0.4	0.2	2.3	1.8	1.5	3.0	3.8	2.8					0.7		0.7	0.4	4.8	3.3		0.004	0.014	0.001	0.003	0.003			0.007	1.0		1.2	0.9	1.6	1.7	1.7	25	14	11	0
		IPR	0.6	0.5	0.8	0.9	0.7	0.7	1.1	1.2					0.6	0.000	0.4	1.3	1.9	0.6		0.001	0.001	0.000	0.001	0.001				0.3		0.7	0.6	1.6	2.0	1.0	25	24	1	0
	Deans switch	KOS_A	1.4	1.2	0.4	0.6	0.4	0.4	0.5	0.6					0.6	0.001	0.7	2.0	0.6	1.8		0.001	0.001	0.002	0.001	0.001			0.001	1.9		0.4	0.4	0.8	3.0	0.8	26	25	1	0
		DOU	2.0	0.8	1.8	1.2	1.8	1.8	4.7	3.5	6.0	7.3		1.9	1.5		1.8	1.5	2.3	4.6	2.7	0.005	0.004	0.004		0.002	0.004		0.003	1.9	0.005	0.9	1.7	4.4	2.5	2.7	28	15	11	2
		YRK	0.3	0.1	0.1	0.3	0.5	0.2	1.6	0.4		0.3		0.8	0.3	0.004	5.4	0.5	0.4	1.5	0.5	0.002	0.003	0.002	0.002	0.002		1.8	0.006	0.2		0.2	0.2	0.9	3.5	0.6	30	25	4	1
GC-FID		RIG	0.3	0.2	1.6	1.8	0.9	0.4	4.7	1.6	4.6	3.2	0.002	3.1	2.1			0.4	1.6	3.3	3.1	0.002	0.003	0.002	0.001	0.002	0.002	1.6	0.009	1.4		1.1	3.8	4.1	6.9	3.2	31	18	13	0
	1 column	HPB_A	0.1	0.2	0.2	0.1	0.2	0.1	0.4	0.3	3.7		0.002	0.2	0.5	0.001	0.3	0.2	0.2	0.1	0.8	0.001	0.001	0.001	0.000	0.000	0.001		0.001	0.6	0.004	0.4	0.2	0.4	0.6	0.7	32	30	2	0
		FZJ_B	1.9	1.2	2.3	1.2	0.7	1.7	2.7	6.9	6.7	1.2	0.003		6.5	0.007		29.5	7.9		2.3					0.002		9.1		9.3		8.0	2.1	5.0	2.7	3.1	24	7	12	5
GC-MS		CMN		1.4	1.7	0.3	1.9	5.7	9.8	9.1					11.3	0.003	8.9		7.7	8.8		0.004	0.049	0.004						0.4		2.0	0.9	4.0	1.4	2.1	21	8	7	6
		FZJ_A			2.6	3.8	1.9	1.0	8.6	4.7					4.2	0.005				2.1		0.003	0.003	0.027	0.019	0.003			0.002			1.9	0.7	1.5	1.0	0.6	20	8	8	4
		HPB_B_MS			0.9	0.6	1.4	1.3	1.5	1.9					2.0	0.001	2.3			0.8		0.001	0.001	0.001	0.001	0.001			0.001			1.5	1.0	1.0	0.8	1.0	21	20	1	0
		PUY							37.2						9.2	0.012													0.011				7.8	8.7	11.5	9.6	8	0	5	3
		SIR							2.7						2.9	0.004													0.004			9.1	1.7	3.1	3.6	3.5	9	1	8	0
		SMR																											0.001			1.9	2.0	1.9	1.8	1.8	6	6	0	0
		JFJ	0.6	1.5	1.6	0.6	1.6	0.9																							0.5	1.6				8	8	0	0
	Medusa	MHD	0.5	0.2	0.3		0.7	1.4																												5	5	0	0
		NILU	1.0	1.0	1.0	1.0	1.0	1.2										1.1	1.0											1.2						9	9	0	0
		N (stations)	15	16	18	17	18	18	17	15	4	4	3	4	17	13	11	12	13	14	5	14	14	14	12	14	4	3	15	14	2	18	19	18	18	17				
		DQOs 1	12	12	13	14	15	14	5	9	0	2	2	3	8	4	5	8	6	6	5	7	4	7	6	9	2	2	7	10	0	13	16	10	7	9				
		DQOs 2	3	2	4	2	2	2	7	3	2	1	1	1	5	8	3	2	7	6	3	5	8	6	5	4	2	1	8	3	2	4	3	8	11	8				
		DQOs 3	0	2	1	1	1	2	5	3	2	1	0	0	4	1	3	2	0	2	0	2	2	1	1	1	0	0	0	1	0	1	0	0	0	0				

PE: PerkinElmer

Table S7: Blank values [pmol/mol] for different compounds submitted from the participants. Empty cells indicate no blank values measured and/or reported. * mole fractions in NMHC_air < 0.1 nmol/mol.

			alkanes															alkenes										alkynes		aromatics				
		station/compounds	ethane	propane	*n*-butane	2-methylpropane	*n*-pentane	2-methylbutane	*n*-hexane	2-methylpentane	3-methylpentane	2,2-dimethylbutane	2,3-dimethylbutane *	cyclohexane	*n*-heptane	*n*-octane *	2,2,4-trimethylpentane	ethene	propene	1-butene	2-methylpropene	*trans*-2-butene *	*cis*-2-butene *	1,3-butadiene *	1-pentene *	*trans*-2-pentene *	*cis*-pentene *	2-methyl-2-butene	isoprene *	ethyne	propyne *	benzene	toluene	ethylbenzene	*m,p*-xylene	*o*-xylene
GC-FID-FID		AUC																																	
		HAR																																	
	Deans switch PE	PAL		38	22	13		5										210	157	172		71	41	113		1				13		24	13			
		SMK								4					3				68	28		15	7	7	5	4			7			17	3	16	29	10
		ZSF	15	15			6	8	4	6							11	118	261	132			41	59	13	6			11			22	78	4	25	25
		IPR			3	2	1								4			35	26	10			2		9							10	2	4		8
	Deans switch	KOS_A					4	9										359	55	30		45	12							79		15			6	
		DOU	35	13	5	11	3	3	1	2					1		3	57	22	5		3	3	3		2				11		4	3	1	1	1
		YRK																								6						4				
GC-FID		RIG																	15					5								17				
		HPB_A																10	2	2	74									12		7				
	1 column	HPB_B			36										2					9				144				171				45	18			
		FZJ_B																																		
		KOS_B																														10	5	2	2	2
GC-MS		CMN		2															2				2									1	1			
		FZJ_A			7											2																27	10	10		9
		HPB_B_MS			57															19				9		16						43	25			
		PUY							4							13												5					48	25	60	36
		SIR							5							2												3				20	33	35	138	24
		SMR																														5	1			
		JFJ																																		
	Medusa	MHD						5																												
		NILU	1																1																	

PE: PerkinElmer

6. Figures

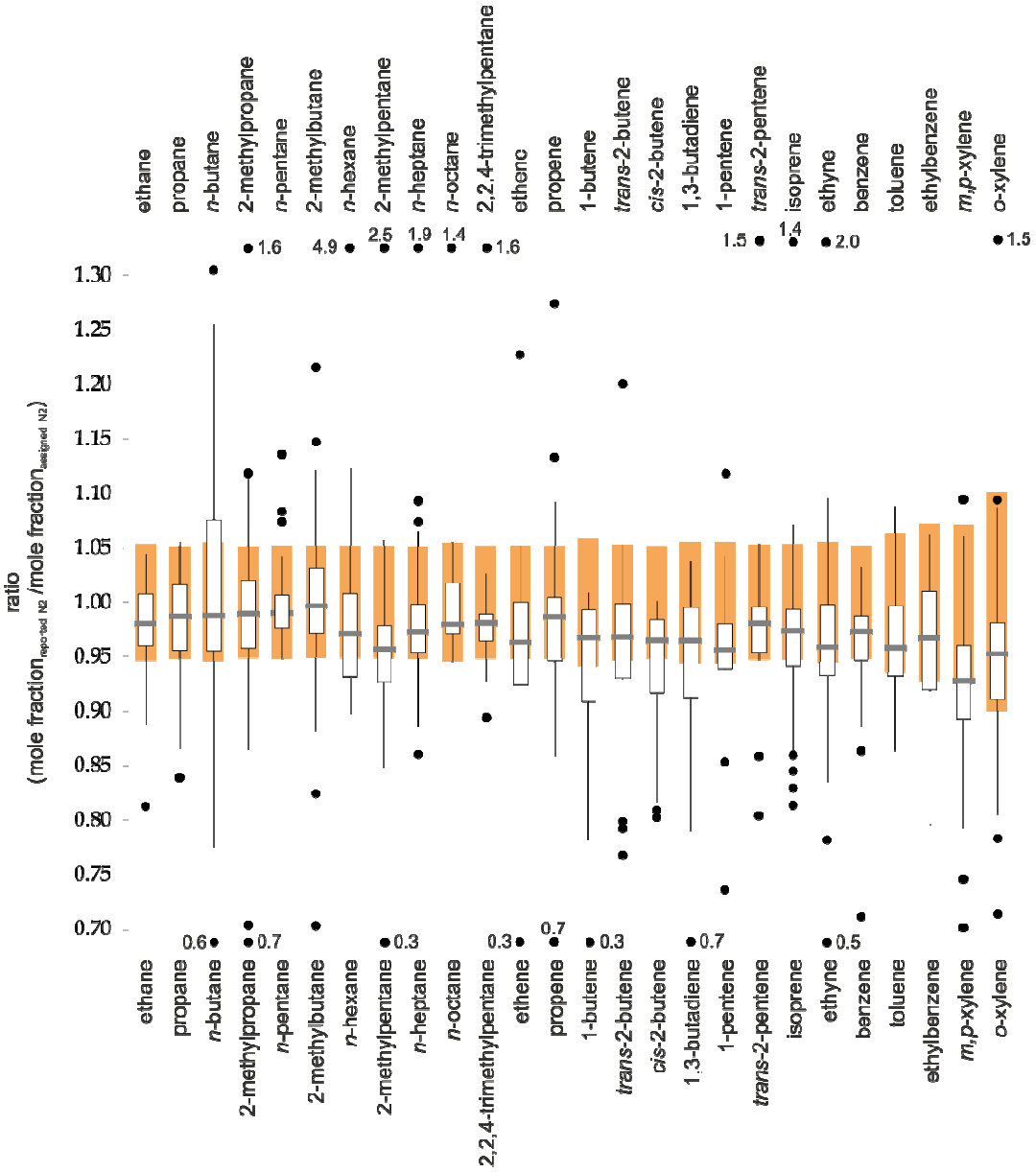


Figure S1: Boxplot of NMHC_N_2 relative to the assigned values (Table 1, main paper). The white box is stretching from the 25th-percentile to the 75th-percentile containing the median in between. The whiskers end at the minimum and maximum observed value or at most 1.5 times the interquartile range. Outliers lower or higher than 1.5 times the interquartile range are represented separately by the dots. The orange box indicates the 5%-class (see Table 2, Equation 1, main paper).

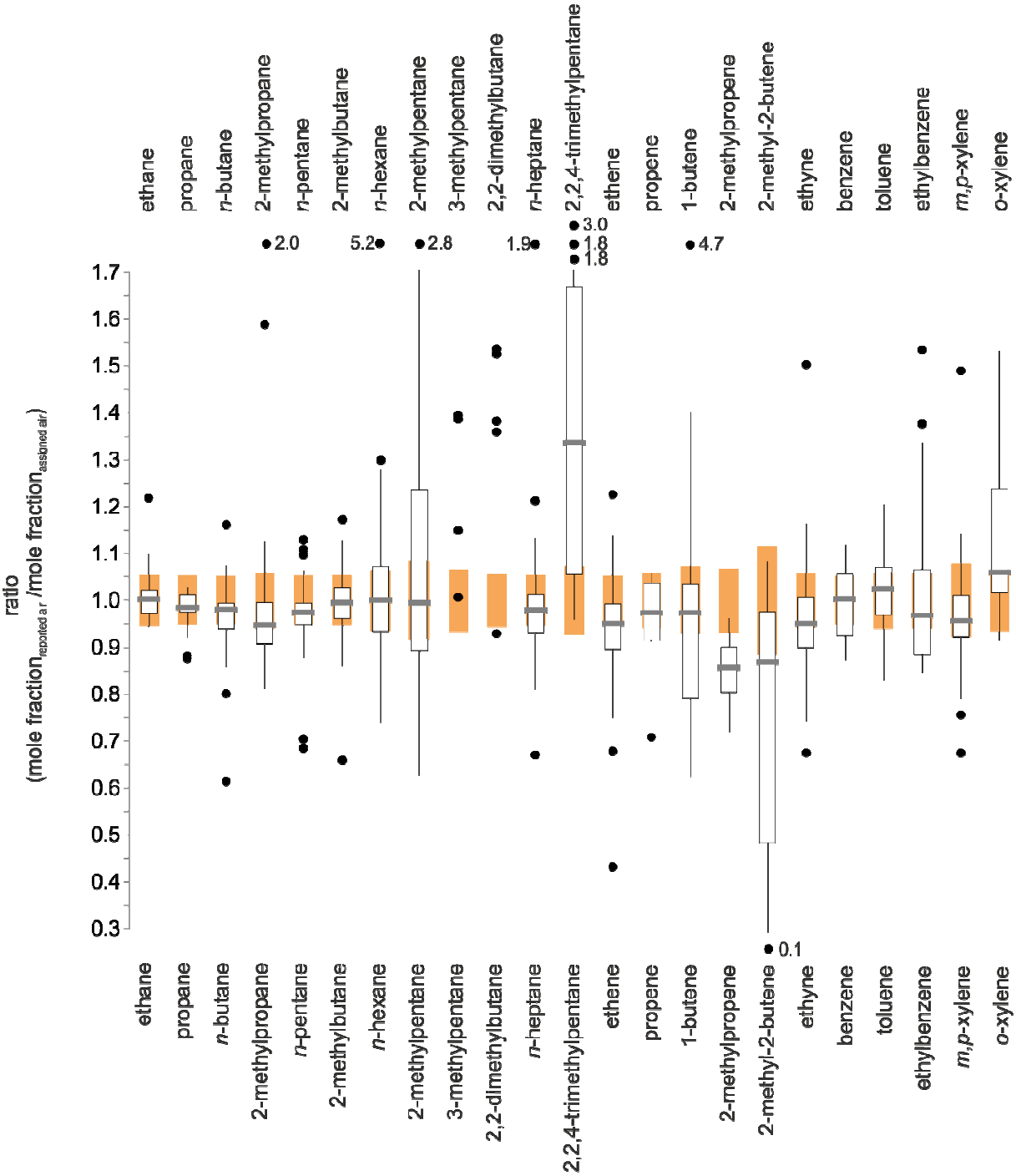


Figure S2: Boxplot of NMHC_air (above 0.1 ppb) relative to the assigned values (Table 1, main paper). The white box is stretching from the 25th-percentile to the 75th-percentile containing the median in between. The whiskers end at the minimum and maximum observed value or at most 1.5 times the interquartile range. Outliers lower or higher than 1.5 times the interquartile range are represented separately by the dots. The orange box indicates the 5%-class (see Table 2, Equation 1, main paper).

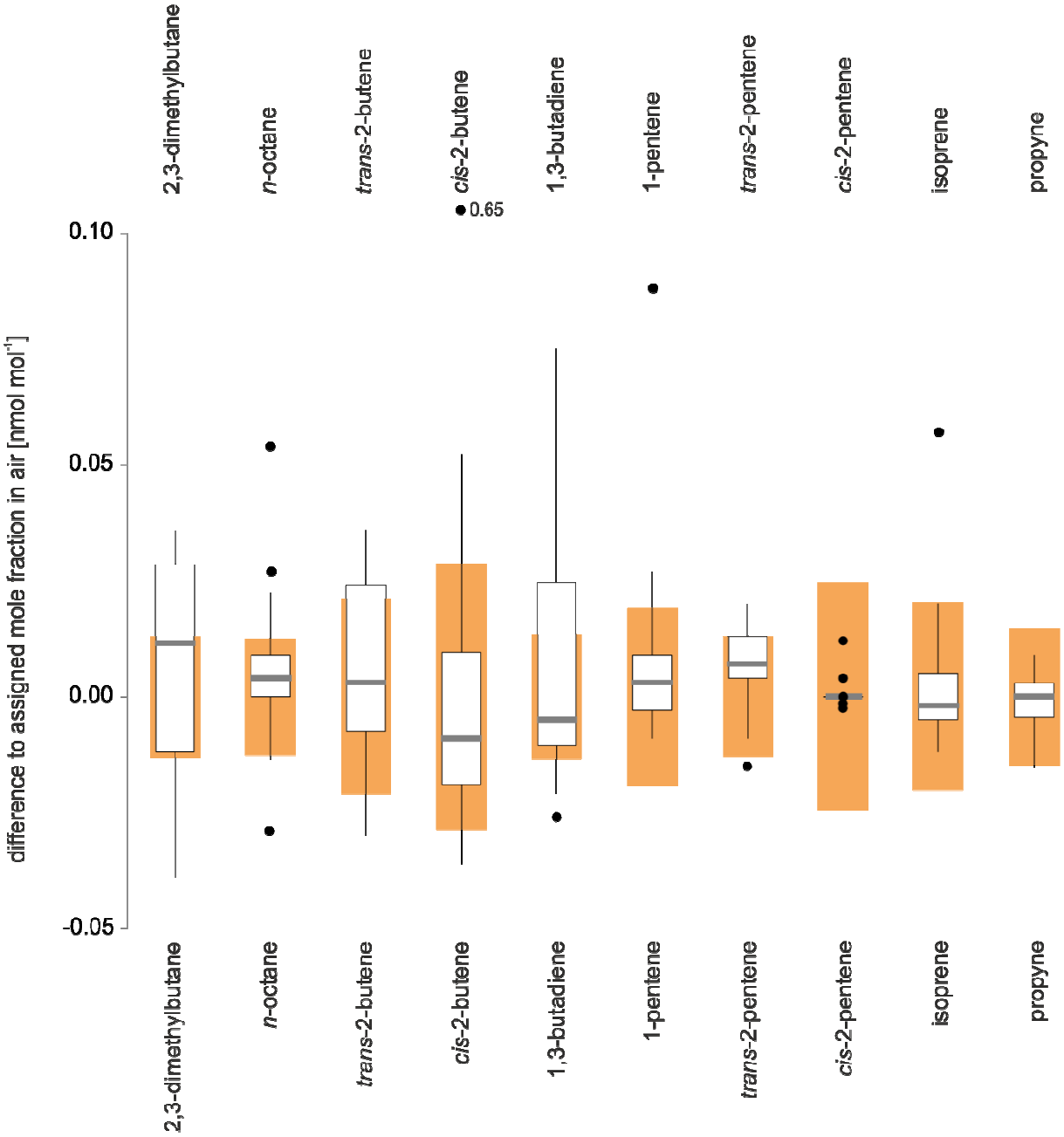


Figure S3: Boxplot of NMHC_air (below 0.1 ppb) relative to the assigned values (Table 1, main paper). The white box is stretching from the 25th-percentile to the 75th-percentile containing the median in between. The whiskers end at the minimum and maximum observed value or at most 1.5 times the interquartile range. Outliers lower or higher than 1.5 times the interquartile range are represented separately by the dots. The orange box indicates the 5%-class (see Table 2, Equation 1, main paper).

Figure S4: Frequency plots of the results in NMHC_N_2 (a-e) and NMHC_air (f-j). On the x-axis the classes of deviations (in %) to the assigned values are indicated. On the y-axis the frequency in % of the different compound groups (as indicated in the legends) are shown. For mole fractions < 100 nmol/mol the classes are in nmol/mol, but for simplicity reasons % are shown (e.g. ±5% corresponds to ±5 nmol/mol). PE= PerkinElmer.

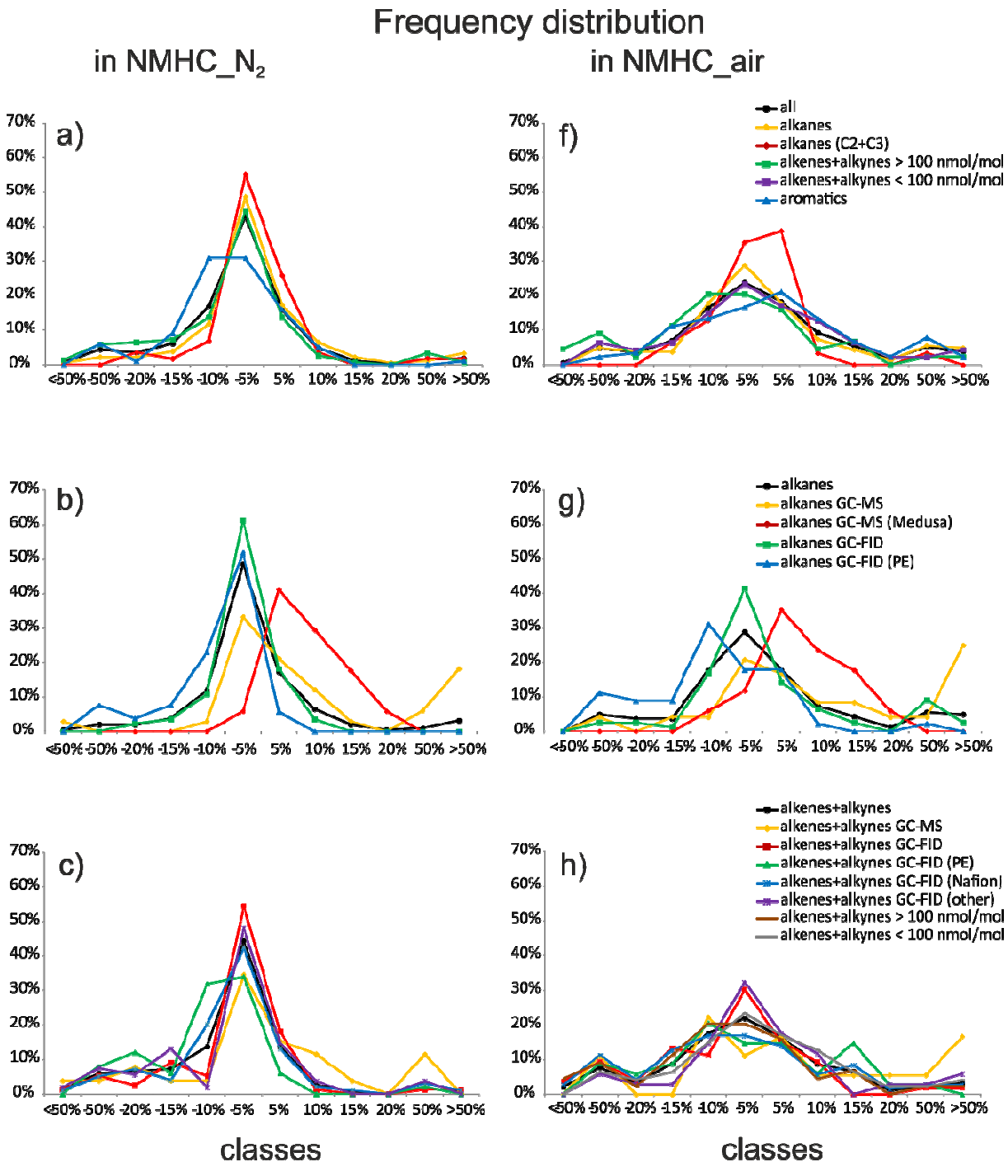


Figure S4 (cont.)

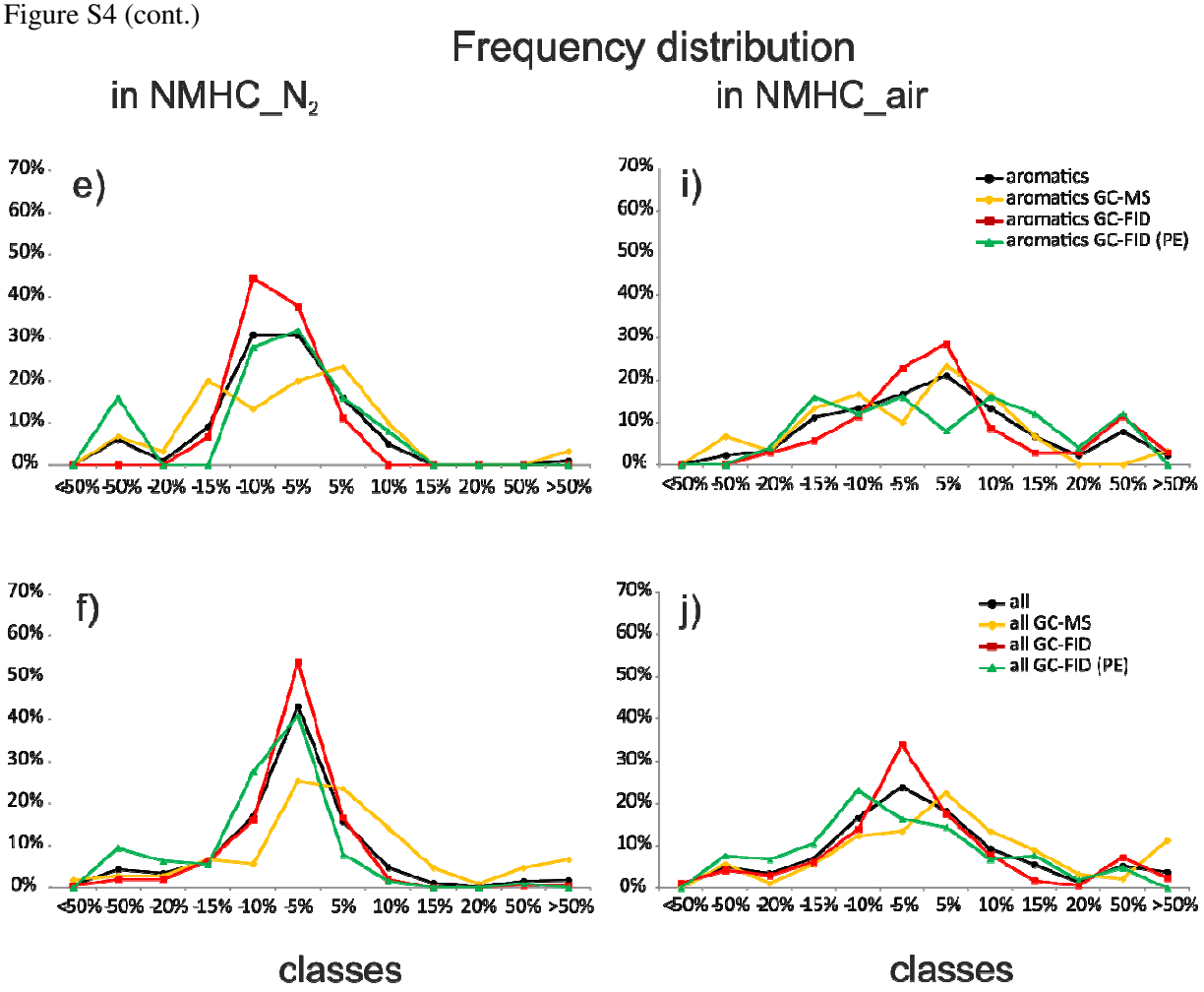
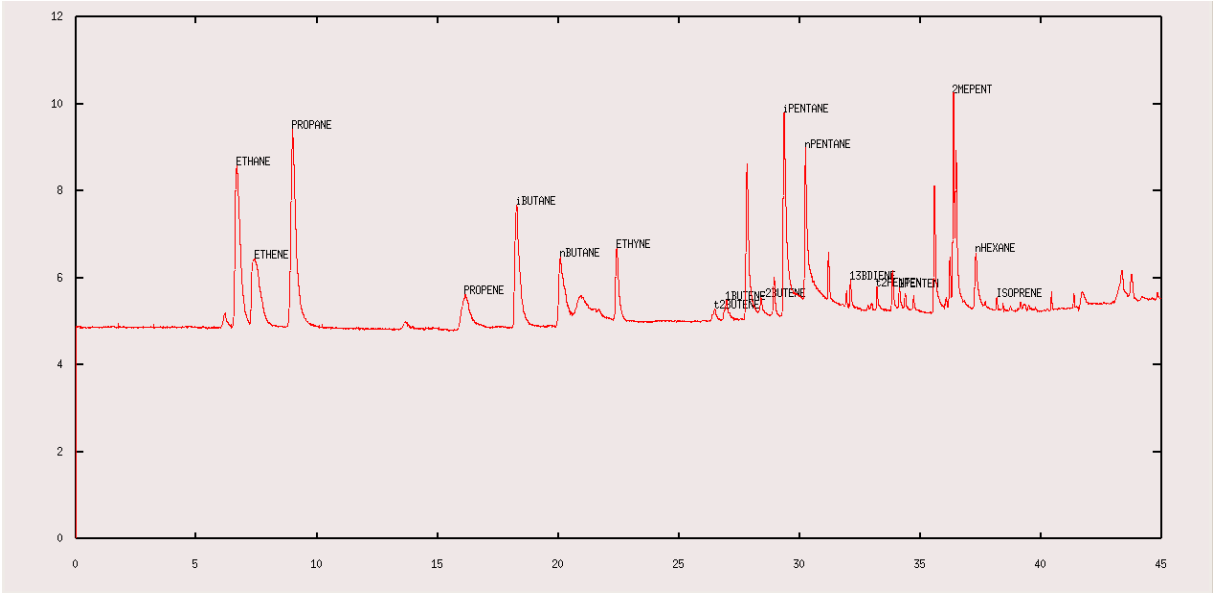
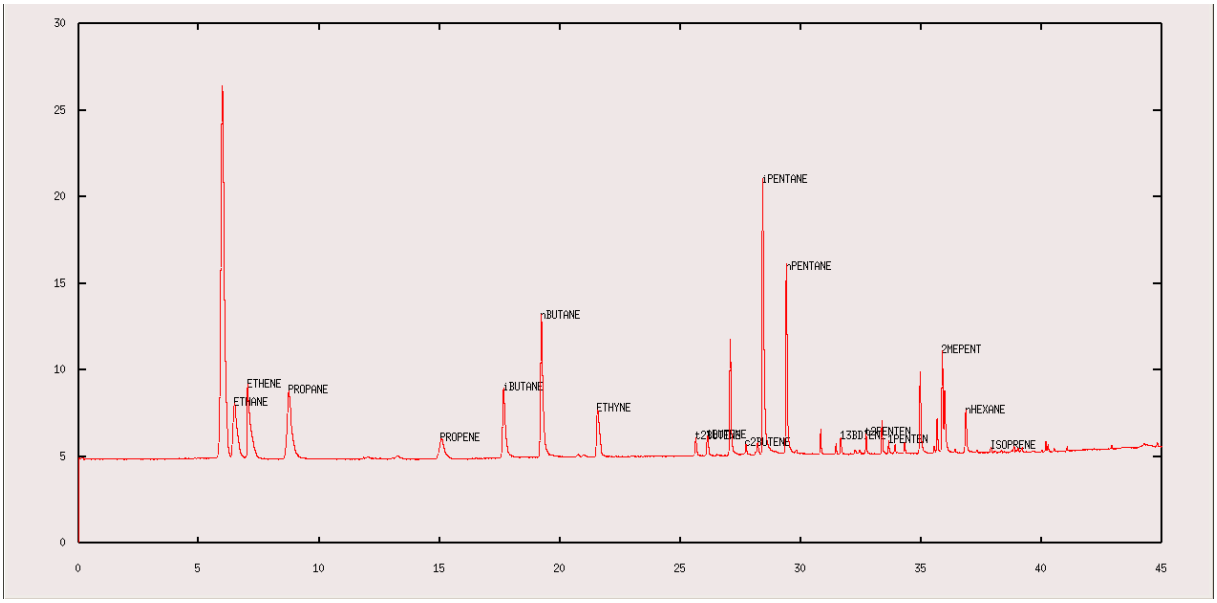


Figure S5: Examples of chromatograms for similar systems at AUC (a) and HAR (b), and for similar systems at (c) KOS_A and (d) PAL.

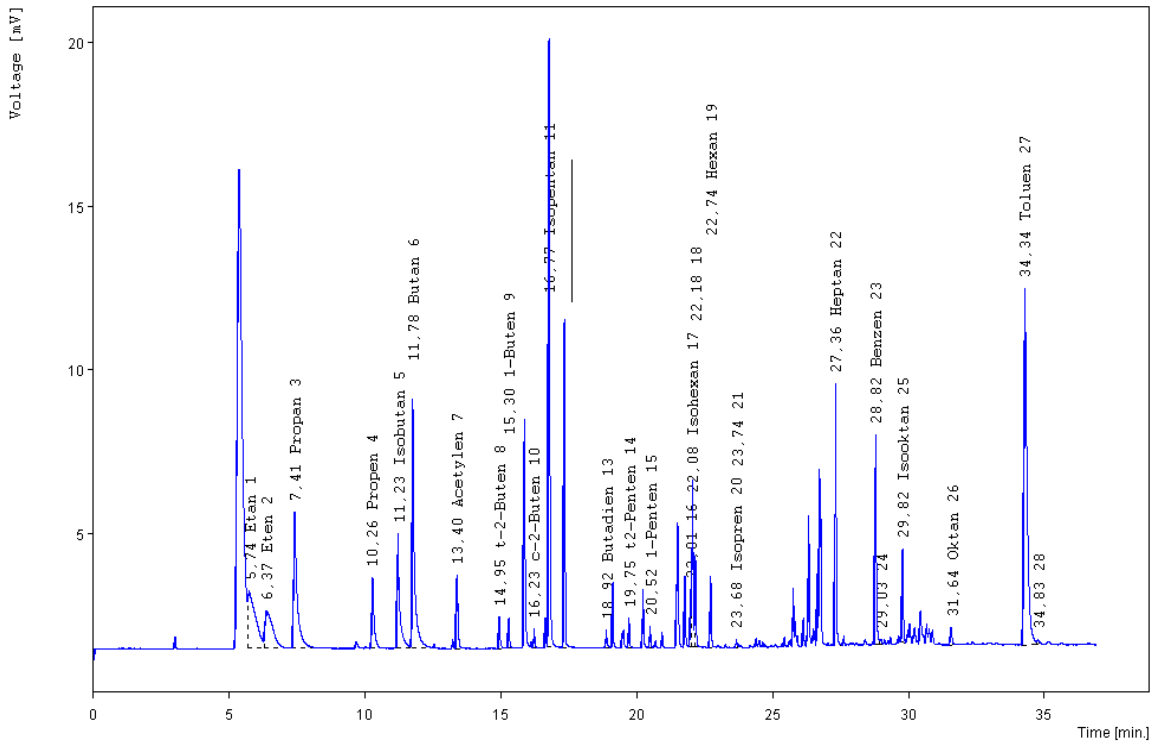
a) Chromatogram in NMHC_air for AUC (PLOT-column).



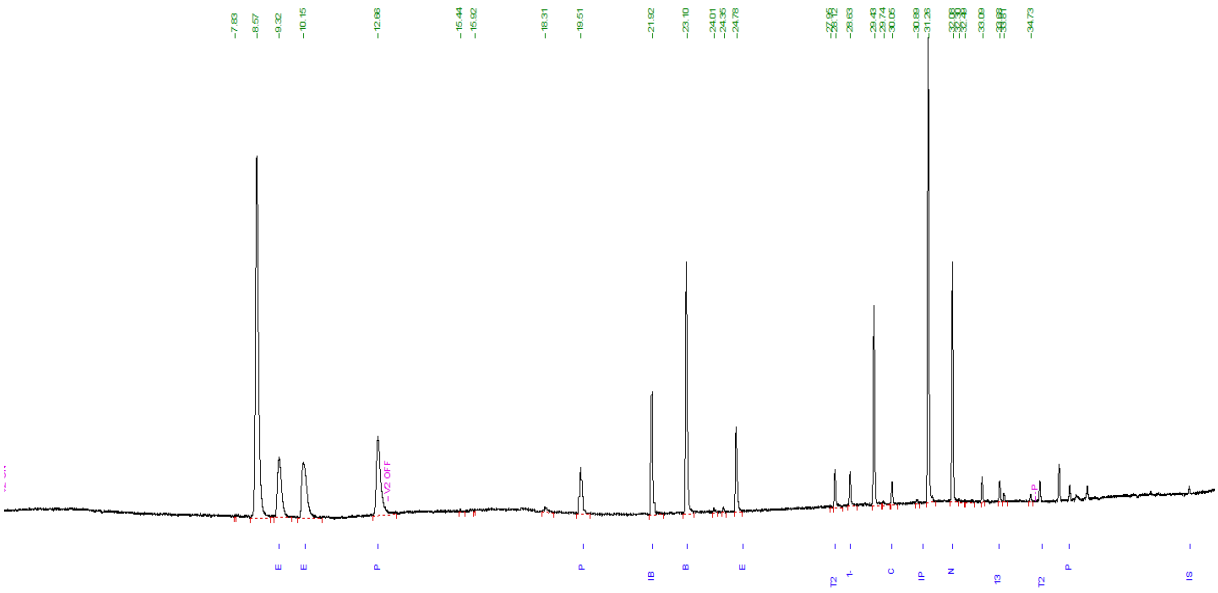
b) Chromatogram in NMHC_air for HAR (PLOT-column).



c) Chromatogram in NMHC_air for KOS_A (PLOT-column).



d) Chromatogram in NMHC_air for PAL (PLOT-column).



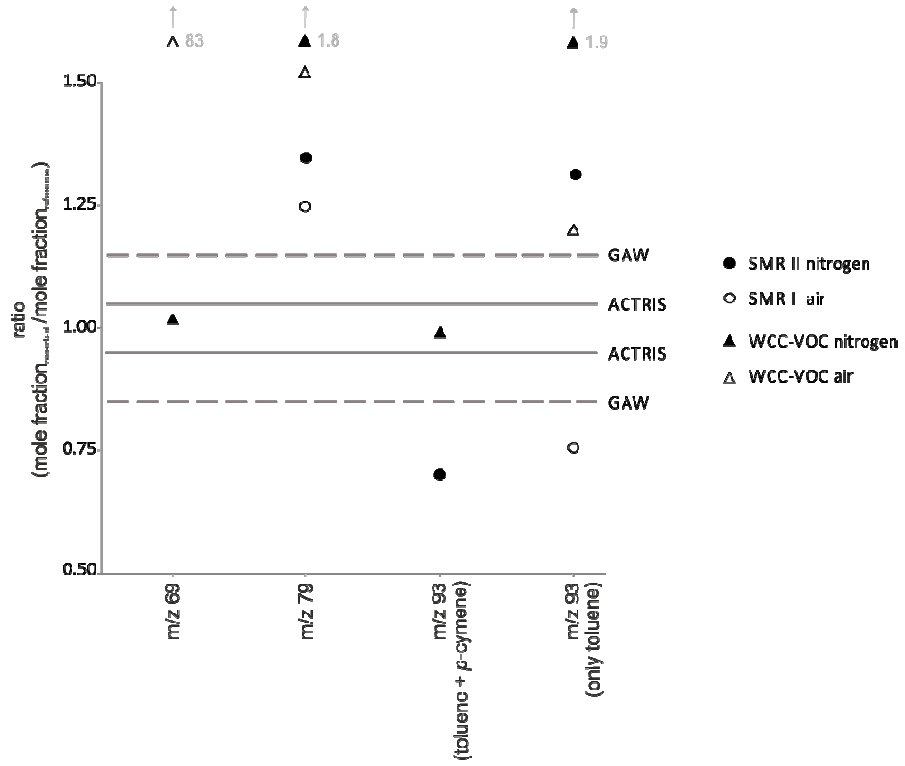


Figure S6: PTR-MS results for m/z 69 (isoprene), m/z 79 (benzene), m/z 93 (toluene + *p*-cymene) and toluene from SMR II and WCC-VOC are presented relative to the reference values. Closed and open circles/triangles indicate results in NMHC_N_2 and NMHC_air, respectively. Solid and dashed grey lines indicate ACTRIS and GAW data quality objectives, respectively (Table 2, main paper).